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Description

The present invention relates in general to an electrochemical device, and more particularly to improvements in an electrochemical device of laminar structure which includes an electrochemical cell using a planar solid electrolyte body.

There have been known various electrochemical devices using solid electrolyte, for example, oxygen sensors to detect the oxygen concentration of an exhaust gas emitted from internal combustion engines of automotive vehicles. The typical examples of such oxygen sensors include an oxygen sensor which comprises a body of oxygen-ion conductive solid electrolyte such as zirconia ceramics and which operates to determine the oxygen concentration according to the principle of an oxygen concentration cell. Also known in the art are electrochemical devices such as sensing and pumping elements for detecting hydrogen, nitrogen, carbon dioxide, etc. In such electrochemical devices, solid electrolyte materials have been generally used in the form of a tubular body which has an elongate bore closed at its one end. In recent years, however, it has been attempted to replace the tubular solid electrolyte body with a solid electrolyte body of planar shape, as disclosed in U. S. Patents Nos: 4,334,974; 4,282,080; and 4,300,990, in view of relatively low productivity and high cost of manufacture of solid electrolyte bodies of tubular type, and from the standpoint of easy assembling of parts with a planar solid electrolyte body. When such planar solid electrolyte bodies are employed, suitable electrodes are disposed on the surfaces of the planar body or layer of solid electrolyte, and the electrolyte bodies and other parts are assembled in stack into a laminar structure constituting an electrochemical cell or sensing element.

As indicated above, such an electrochemical cell of laminar structure is usually constituted by a planar solid electrolyte body and two (a pair of) electrodes. This laminar structure is provided with an internal cavity or chamber into which a gas to be measured (hereinafter referred to as "measurement gas") such as an exhaust gas is introduced. The laminar structure is further provided with an internal space, more specifically, a reference-gas passage in which is introduced a reference substance used as a reference for the measurement gas for measuring an electromotive force induced between the two electrodes. These cavity and reference-gas space or passage are formed so as to extend parallel to the surfaces of the electrodes, but disposed in spaced-apart relation with each other in the direction of the thickness of the cell (in the direction of lamination of the device), and therefore increase the thickness of the cell.

A study by the inventors revealed that an electrochemical sensor using such a thick cell tends to have a relatively large temperature gradient in the direction of thickness, particularly when its solid electrolyte body is heated, by a suitable heater, to an elevated temperature for accurate and reliable operation of the cell, and consequently the solid electrolyte body is likely to be damaged due to thermal stress caused by such a large temperature gradient. In addition to this problem, the inventors found that the large thickness of the cell is a potential factor for an increase in time required for the solid electrolyte body to be heated to its operating temperature. Although electrochemical cells of planar laminar type are advantageous for its relatively compact structure, as compared with a conventional cell of tubular type, there is a growing need of minimizing the size of the planar electrochemical cells, to meet the recent trend in this field of industry that the electrochemical cells are increasingly employed for automotive vehicles as oxygen sensors for sensing oxygen in exhaust gases from the engines.

As indicated above, it is usually preferred that the electrodes and solid electrolyte body constituting an electrochemical cell of the electrochemical device are heated by a suitable heater to an elevated temperature in order to assure an efficient, accurate operation of the electrochemical cell while the temperature of a gas to be measured is relatively low. For this reason, a known electrochemical device is provided with a heater, i.e., a heating layer, which is disposed adjacent to an electrochemical cell consisting of a solid electrolyte body and electrodes, such that an insulating layer is interposed between the heater and the electrochemical cell. Alternatively, a heater is disposed at a position spaced from the electrodes in the same plane of the electrochemical cell.

One example of electrochemical devices of laminar structure as indicated above, includes an electrochemical pumping cell which has two porous electrodes disposed on opposite surfaces of a porous solid electrolyte layer, and an electrochemical sensing cell which has two porous electrodes disposed on another solid electrolyte layer. These pumping and sensing cells are assembled in stack into an electrochemical device of laminar structure. This kind of device is known to be useful as a sensor having a wide measurement range. In the case where such an electrochemical device is provided with a heater as previously indicated, the heater is generally disposed on the side of the sensing cell. If a heater is disposed on the side of the pumping cell, a pattern of heating element located over the pumping electrodes will tend to excessively heat the electrodes and cause local unevenness in diffusion of a measurement gas

through the pumping cell, and may consequently reduce the accuracy of measurement of the device. In the case where the heating element is not disposed over the electrodes, but located sideways of the electrodes to heat them in the lateral directions, the temperature of the heated electrodes is liable to be varied from one area to another, causing local unevenness in amount flow of pumping current through the cell. This may also be a cause for lowering the measuring accuracy of the electrochemical device.

However, when a heater is disposed on the side of an electrochemical sensing cell, this sensing cell is interposed between the heating element and the electrodes of a pumping cell. The interposition of the sensing cell permits better distribution of heat over the pumping cell. Further, this arrangement will not hinder the diffusion of the measurement gas through the pumping cell. On the other hand, the interposition of the sensing cell between the pumping cell and the heater inherently results in insufficient heating of the pumping cell by the heater, and therefore the use of the heater does not necessarily contribute to improvement in the pumping ability of the pumping cell. In the light of this disadvantage, it is considered to use a heater having a larger heating capacity for generation of an increased amount of heat. Such a solution, however, may lead to shortening of the service life of the heating layer of the electrochemical device.

GB-A-2 054 868 discloses an oxygen sensor which has a reference electrode and a measuring electrode in a common plane on a solid electrolyte carrier. These electrodes are exposed to gases contained in grooves in an opposing plate. For the measurement gas, the grooves provide predetermined diffusion resistance.

DE-A-2736451 shows an oxygen sensing cell, having a planar solid electrolyte with a measuring electrode on one side exposed to the gas to be measured, and two electrodes on its other side, exposed to an atmosphere containing oxygen from an oxygen source. One of these two electrodes is employed as a measuring electrode, and the other as a transfer electrode for pumping oxygen from the reference chamber to the measuring electrode.

GB-A-2050625 discloses another device for detection of oxygen concentration in combustion gas, having two oxygen ion conductive solid electrolytes sandwiched with three electrodes. One of these solid electrolyte layers is porous. The exhaust gas being measured directly contacts the outer two electrodes and also contacts the middle electrode through the porous electrolyte. The porous electrolyte is part of a pumping cell, while measurement is taken across the other electrolyte. In another embodiment in this document, there is only a

single cell, and a heater is provided in alignment with the electrodes of that cell.

JP-A-58-153155 (corresponding to US-A-4450065) discloses an oxygen sensor having an oxygen pumping cell and an oxygen concentration (sensing) cell, each having two electrodes, with all four electrodes in alignment with each other. In one embodiment, a heater is provided.

The present invention was developed in the light of the above prior art. It is therefore an object of the present invention to provide a compact electrochemical device including an electrochemical cell which has a reduced thickness and consequently a reduced temperature gradient in the direction of thickness.

The present invention is set out in claim 1.

In the electrochemical device of the invention the reference electrode is spaced from the measuring electrode in the direction along the surface of the second solid electrolyte body, and the heating element of the heater is aligned with the measuring electrode. Therefore, the reference electrode will not intercept the heat from the heater toward the pumping electrodes of the pumping cell. Usually and preferably, a reference-gas passage is formed so that the reference electrode is exposed to a reference gas introduced in the reference-gas passage. In this instance, the spaced-apart arrangement of the reference electrode from the measuring electrode makes it possible to position the heating element in spaced relation with the reference-gas passage in the direction parallel to the surface of the second solid electrolyte body. Therefore, the heat transfer from the heating element toward the pumping electrodes will not be hindered by the reference-gas passage.

Embodiments of the present invention will be given by way of example in the following description in conjunction with the accompanying drawings in which:-

Fig. 1 is an exploded perspective view of a sensing element of one embodiment of an electrochemical device of the invention in the form of an oxygen sensor;

Fig. 2 is a schematic elevational view in cross section taken along line 2-2 of Fig. 1;

Fig. 3 is a view corresponding to Fig. 1, showing a modified form of an oxygen sensor similar to the sensor of Fig. 1;

Fig. 4 is a cross sectional view of the oxygen sensor of Fig. 3, taken along line 3-3 of Fig. 3; and

Fig. 5 is a view corresponding to Figs. 2 and 4, showing a further modified form of an oxygen sensor similar to those of Figs. 1 and 3.

Referring to the accompanying drawing illustrated preferred embodiments of the present invention, the arrangement of an electrochemical device

suitable for implementation of the invention will be described in detail.

In the exploded perspective view of Fig. 1, there is illustrated a basic arrangement of an oxygen concentration sensing element embodying the invention. Fig. 2 shows the sensing element in longitudinal cross section, in enlargement in the direction of thickness of the sensing element. This oxygen concentration sensing element (oxygen sensor) is one of so-called "lean-burn sensors", which is an integral co-fired laminar structure comprising an oxygen pumping cell 202, an oxygen concentration sensing cell 204, and a heater 206, with the sensing cell 204 sandwiched by the pumping cell 202 and the heater 206.

The oxygen pumping cell 202, which is one component of the sensing element, includes a planar porous body 208 of oxygen-ion conductive solid electrolyte (first solid electrolyte body 208) which is made, for example, of zirconia ceramics containing yttria. The planar porous solid electrolyte body 208 has a porous outer pumping electrode 210 on one of its opposite surfaces, i.e., on the surface exposed to a measurement gas such as an exhaust gas. The outer pumping electrode 210 is made, for example, of platinum-zirconia. On the other surface (inner surface) of the porous solid electrolyte body 208, there is disposed an inner pumping electrode 212 which is aligned with the outer pumping electrode 210. This inner pumping electrode 212 is made of the same material as the outer pumping electrode 210, that is, made of porous platinum-zirconia. The pumping electrodes 210, 212 are connected to an external power source 214 through their leads, so that a predetermined amount of electric current flows between the two electrodes 210, 212.

The porous solid electrolyte body 208 functions as a diffusion-resistance layer through which a selected component, for example, oxygen, of the measurement gas is diffused from one surface thereof to the other surface. The pores in the solid electrolyte body 208 provide a predetermined diffusion resistance to molecules of the selected component. In this electrochemical pumping cell 202 consisting of the porous solid electrolyte body 208 and the pair of pumping electrodes 210, 212 on the outer and inner surfaces of the body 208, the oxygen in the measurement gas is diffused to the side of the inner pumping electrode 212 through the porous structure of the solid electrolyte body 208, and the oxygen around the inner pumping electrode 212 is pumped out toward the outer pumping electrode 210 and discharged into the outside measurement gas by means of a well known pumping action by applying a suitable voltage between the two electrodes 210, 212. The amount of oxygen to be discharged is varied in

proportion to the amount of an electric current flowing through the electrodes 210, 212.

Unlike the oxygen pumping cell 202, the oxygen sensing cell 204 uses a planar gastight body 216 of solid electrolyte made of zirconia ceramics containing yttria, or the like. On the inner surface of the gastight solid electrolyte body 216, i.e., on the surface on the side of the pumping cell 202, there are disposed a porous measuring electrode 218 and a porous reference electrode 220, such that the measuring electrode 218 is aligned with the inner pumping electrode 212 and exposed to the atmosphere existing in the vicinity of the inner pumping electrode 212, and such that the measuring and reference electrodes 218 and 220 are juxtaposed in spaced-apart relation with each other. As described later, the reference electrode 220 is protected by gastight ceramic layers from exposure to the measurement gas. Thus, the second solid electrolyte body 216 and the measuring and reference electrodes 218, 220 constitute an electrochemical cell in the form of the oxygen concentration sensing cell 204.

Between the measuring electrode 218 of the sensing cell 204 and the inner pumping electrode 212 of the pumping cell 202, there is interposed a thin porous ceramic layer 222 made of alumina or zirconia, or the like. Through this porous ceramic layer 222, the electrodes 212 and 218 are concurrently exposed to the same atmosphere. In other words, the measuring electrode 218 is exposed to the atmosphere which is controlled by the previously indicated pumping action, and which exists around the inner pumping electrode 212. A gastight ceramic layer 224 of zirconia or like material having a high electric resistance is interposed between the pumping cell 202 and the gastight solid electrolyte body 216, so as to cooperate with the solid electrolyte body 216 to sandwich the reference electrode 220 which is spaced from the measuring electrode 218. In other words, the reference electrode 220 is embedded or encapsulated by the two gastight ceramic layers 224, 216, and thereby protected from exposure to the measurement gas.

These measuring and reference electrodes 218, 220 are connected through their leads to a suitable external measuring device (potentiometer 226) for measuring an electric potential between the two electrodes. Stated in detail, the oxygen concentration sensing cell 204 is adapted to measure an electromotive force based on a difference in concentration of oxygen between the reference electrode 220 which is held at a high potential of oxygen concentration by a separate pumping action, and the measuring electrode 218 which is contacted with the atmosphere which exists around the inner pumping electrode 212 and contains the controlled amount of oxygen from the outside mea-

surement gas. Reference numerals 228 and 230 in Fig. 1 indicate a power source and a resistor incorporated in the electromotive force measuring circuit. With a voltage applied with the power source 228 between the inner pumping electrode 212 and the reference electrode 220, the oxygen component is transferred from the inner pumping electrode 212 to the reference electrode 220 which has the porous structure. With this separate pumping action, the oxygen component is accommodated as a reference gas in the porous structure of the reference electrode 220. That is, the reference electrode 220 is contacted with the reference gas existing in its pores. Thus, the pores in the reference electrode 220 serves as a reference-gas space.

The heater 206 is disposed in contact with the outer surface of the oxygen concentration sensing cell 204, i.e., on the surface remote from the oxygen pumping cell 202 and opposite to the surface on which the electrodes 218, 220 are disposed. The heater 206 consists of an integral assembly of a ceramic layer 238 made of zirconia or the like, and a heating element 234 and its leads 236, which are formed on the ceramic layer 238. The heater 206 is attached to the outer side of the sensing cell 204, so that the heating element 234 is aligned with the measuring electrode 218 which are aligned with the outer and inner pumping electrodes 210, 212. Heat is generated from the heating element 234 upon energization thereof with DC power supplied through the leads 236 from an external power source.

In the electrochemical device (sensing element) of Figs. 1 and 2 wherein the heater 206 is not directly contact with the pumping cell 202, but positioned in close proximity with the oxygen concentration sensing cell 204, the diffusion of the oxygen component through the pumping cell 202 is not affected by the pattern of the heating element 234. Further, since the heating element 234 is formed so as to cover the entire area of the pumping electrodes 210, 212 and their vicinities, the pumping electrodes 210, 212 are heated uniformly over the entire surfaces with even heat distribution.

While the oxygen pumping cell 202 is heated by the heater 206 via the oxygen concentration sensing cell 204, the reference electrode 220 is disposed so as not to overlap the measuring electrode 218, that is, the reference electrode 220 is spaced from the measuring electrode 218 so that the reference electrode 220 will not intercept the heat from the heater 206 toward the pumping cell 202. Accordingly, the pumping cell 202, more particularly, their electrodes 210, 212 are more effectively heated by the heater 206. In other words, the spaced-apart arrangement of the measuring and reference electrodes 218, 220 of the sensing cell

204 allows increased efficiency of heat transfer from the heater 206 to the pumping cell 202, thereby improving the pumping ability of the pumping cell and prolonging its service life.

In the case where a suitable reference-gas space is formed adjacent to the reference electrode 220, the spaced-apart positioning of the reference electrode 220 relative to the measuring electrode 218 is particularly effective, because such a space is not formed on the heat transfer path from the heating element 234 toward the pumping electrodes 210, 212.

A further advantage of the present electrochemical device lies in the fine porous structure of the solid electrolyte body 208 of the pumping cell 202, which porous structure functions as a diffusion-resistance layer through which the oxygen in the outside measurement gas is diffused toward the inner pumping electrode 212. This arrangement for introducing the oxygen into the interior of the device is less liable to suffer a trouble of timewise variation in diffusion resistance due to accumulation of soots or other substance on the cell, as compared with a conventional arrangement wherein a pin hole or leak aperture is formed as a diffusion hole for communication between the outside atmosphere (measurement gas), and a cavity formed within the device.

In the electrochemical device with the above-described construction, the oxygen partial pressure (concentration) of the atmosphere with which the measuring electrode 218 of the sensing cell 204 contacts, is controlled by way of a pumping action of the pumping cell 202 and by means of a diffusion resistance of the porous solid electrolyte body 208 serving as a diffusion-resistance layer, so that the oxygen partial pressure in question is made lower than that of the outside measurement gas. Consequently, the electrochemical oxygen sensor is suitably used as a lean-burn sensor for controlling an engine which emanates an exhaust gas of lean air-fuel ratio whose oxygen partial pressure is higher than that of the stoichiometric air-fuel ratio.

The planar solid electrolyte bodies 208, 216 of the pumping and sensing cells 202, 204 may be made of other ceramic materials than zirconia ceramics, e.g. aluminium nitride, SrCeO_3 , solid solution of bismuth oxide and oxide of rare earth element or $\text{La}_{1-x}\text{Ca}_x\text{YO}_{3-\alpha}$. As stated before, the solid electrolyte body 208 of the pumping cell 202 should be porous because it serves as a diffusion-resistance layer having a predetermined diffusion resistance to molecules of a selected component of a measurement gas. The porosity of the porous structure of the solid electrolyte body 208 is suitably selected depending upon the required level of diffusion resistance, and upon a specific method of fabrication of the body 208. If the body 208 is

fabricated in a sintering process, for example, the porosity is preferably held within a range of approx. 2-30% as measured according to a mercury porosimetric method (measured by Mercury Porosimeter Type 70H made by Carlo Erba, Italy). If a plasma spraying process is used to manufacture the body 208, the preferred porosity range is 0.5-10% as measured with the same method.

The ceramic layer 222 interposed between the inner pumping electrode 212 of the pumping cell 202 and the measuring electrode 218 of the sensing cell 204, should be a porous layer, preferably a thin porous layer, since the electrodes 212 and 218 are exposed to the same atmosphere through this ceramic layer. The gastight ceramic layer 224 which cooperates with the solid electrolyte body 216 to gas-tightly enclose the reference electrode 220, may be made of various known ceramic materials such as zirconia, alumina, mullite, spinel, titania, barium titanate and calcium zirconate. Among these ceramics, zirconia is most preferably used as a major component of the gastight ceramic layer 224.

The ceramic layer 238 supporting the heating element 234 and leads 236 of the heater 206 is preferably a gastight layer made of ceramic materials indicated above for the gastight ceramic layer 224. The heating element 234 and leads 236 are layers which are made of a mixture of at least one element selected from the platinum group consisting of platinum, palladium, rhodium, iridium, ruthenium and osmium, and ceramics such as zirconia, yttria and alumina. Accordingly, the adhesion between the heating element and leads 234, 236 of the heater 206, and the surrounding ceramic layers 216, 238 is appreciably improved. In preparing a mixture material for forming the heating element and leads by firing, it is advantageous to admix fine particles of the above indicated ceramic material with a mass of powder of the above indicated platinum group.

For improving the adhesion of the electrodes 210, 212, 218 and 220 of the cells 202, 204, and their leads, it is also preferred to use a mixture of the above indicated platinum group element(s) and ceramics which are suitably used for the heater components (234, 236), as indicated before.

For manufacturing the electrochemical oxygen sensor of laminar structure consisting of the pumping cell 202, sensing cell 204 and heater 206 which have been described, known methods are employed. For example, the electrodes and their leads are first printed, as by a screen-printing method, on green sheets of the solid electrolyte bodies 208, 216. In the meantime, the porous ceramic layer 222 and gastight ceramic layer 224 are formed by printing on one of the pumping and sensing cells 202, 204, while the heating element and leads 234,

236, and the ceramic layer 238 are printed in order on the outer surface of the solid electrolyte body 216 of the sensing cell 204. The prepared assembly of the pumping cell 202, and the prepared assembly of the sensing cell 204 with the heater 206, are assembled in stack into a laminar structure and co-fired into the intended electrochemical sensing element. For improved strength of the sensing element, however, it is possible to first co-fire the laminated assembly without the porous solid electrolyte body 208, and then form the porous solid electrolyte body 208 in a plasma spraying process.

An example of modified form of construction is illustrated in Figs. 3 and 4.

Unlike the preceding arrangement, an electrochemical device shown in Figs. 3 and 4 uses a single electrode member which commonly serves as the inner pumping electrode 212 of the pumping cell 202, and as the measuring electrode 218. Thus, the sensor is simplified in construction, and comparatively economical to manufacture.

The gastight solid electrolyte body 216 of the sensing cell 204 cooperates with a spacer member 242 and a covering member 244 both made of a gastight ceramic material, to define a reference-gas passage 246 which is open at one end to the ambient atmosphere. The reference electrode 220 is located such that it is exposed to the atmosphere introduced in the reference-gas passage 246. This is an outstanding feature of this modified construction. Described in greater detail, the spacer member 242 has an elongate cutout (slot) 248, and is covered on its opposite sides by the upper covering member 244 and the lower pumping and sensing cells 202, 204, so that the reference-gas passage 246 is formed as shown in Fig. 4. This reference-gas passage is in communication with the ambient atmosphere through the opening at one end of the cutout 248 in the spacer member 242. In contrast to the preceding device, the present electrochemical device uses the ambient atmosphere as a reference atmosphere to which the reference electrode 220 is exposed. Due to a difference in concentration of oxygen between the ambient atmosphere in the reference-gas passage 246, and the controlled atmosphere of the measurement gas in the vicinity of the measuring electrode 218, an electromotive force is generated between the measuring and reference electrodes 218 and 220, and measured in the known manner.

A gas-inlet aperture 250 is formed through portions of the spacer and covering members 242, 244 in alignment with the outer pumping electrode 210. Between the spacer member 242 and the outer pumping electrode 210, there is interposed a porous electrode protective layer 252 made of alumina. The outside measurement gas is introduced

to the outer pumping electrode 210 through the gas-inlet aperture 250 and through the porous electrode protective layer 252, in a direction normal to the plane of the pumping electrode 210. Stated the other way, the gas-inlet aperture 250 in the gastight ceramic layers 242, 248 over the outer pumping electrode 210 functions as a gas-inlet layer to control the direction of entry of the outside measurement gas, so that the gas is directed perpendicularly to the surface of the diffusion-resistance layer of the porous solid electrolyte body 208, that is, to prevent the measurement gas from reaching the outer pumping electrode 210 laterally of its surface. In this arrangement, the measurement gas whose flow is controlled by the aperture 250 is diffused through the electrode 210 and the porous solid electrolyte body 208 in the direction normal to their surfaces, whereby the amount of gas to be introduced can be suitably controlled.

In this connection, it is noted that the porous structure of the solid electrolyte body 208 serves as diffusion-resistance means having a predetermined resistance to molecules of oxygen in the measurement gas, and further functions as a measurement-gas space to which the inner pumping electrode 212 and the measuring electrode 218 are exposed. It is further noted that this measurement-gas space (porous structure 208) and the reference-gas passage 246 are juxtaposed in spaced-apart relation in substantially the same plane. Therefore, the thickness of the oxygen sensor is reduced.

In the present modified sensor, the heating element 234 and leads 236 of the heater 206 are sandwiched by gastight ceramic layers 238 and 240 made of zirconia or the like having a high electric resistance. The heater 206 is attached to the outer surface of the sensing cell 204 via an insulating layer 232 made of porous alumina or like material, and connected to an external DC power source. Reference numerals 254, 256, 258 indicate insulating layers of porous alumina or the like, which electrically insulate the leads for the electrodes, like the electrode protective layer 252 for insulation of the outer pumping electrode 210.

In this illustrated arrangement wherein the reference electrode 220 is exposed to the reference-gas passage 246, the spaced-apart positioning of the reference electrode 220 relative to the measuring electrode 218 prevents the reference-gas passage 246 from being interposed between the pumping electrodes 210, 212 and the heating element 234 of the heater 206 and thereby intercepting the heat from the heater. Thus, the effect of the spaced-apart arrangement of the electrodes 218, 220 is more prominent than in the preceding arrangement.

Although the measuring and reference elec-

trodes 218, 220 of the sensing cell 204 are disposed on the same surface (inner surface) of the gastight solid electrolyte body 216, it is possible that these two electrodes 218, 220 are provided on the opposite surfaces, respectively. An example of such a modification is illustrated in Fig. 5.

In this modified sensor, the reference electrode 220 is disposed on the outer surface of the solid electrolyte body 216 of the sensing cell 204, and exposed to a reference-gas passage 246 which is similar to the passage 246 of the preceding sensor. Described more specifically, the inner ceramic layer 240 of the heater 206 has an elongage cutout (slot) similar to that formed in the spacer member 242 of the preceding sensor, and the outer ceramic layer 238 is adapted to serve as a covering member like the covering member 244 of the preceding embodiment. Further, the electrically insulating layer 232 has a cutout similar to that provided in the ceramic layer 242. With these members 238, 240 and 232 stacked on the outer surface of the solid electrolyte body 216, there is formed the reference-gas passage 246 which is open at one end to the ambient atmosphere, and in which the reference electrode 220 is located such that it is substantially completely protected from exposure to the measurement gas by the gastight ceramic layers 238, 240.

As the other parts of the instant modified form of the sensor are functionally identical to those of the aforementioned sensors, the same reference numerals have been used to identify the corresponding parts, and a repeated detailed description thereof is omitted herein.

As is apparent from the foregoing description, the electrochemical devices of Figs. 1-5 according to the invention comprise a laminated assembly of electrochemical pumping and sensing cells, and a suitably constructed heater which is disposed on the side of the electrochemical sensing cell. The device is characterized in that the reference electrode exposed to a predetermined reference atmosphere is spaced from the measuring electrode exposed to the controlled atmosphere of the measurement gas, in a plane of vertical elevation perpendicular to the plane of lamination of the device. In this arrangement, the transfer of heat from the heater toward the pumping cell is not hindered by the reference electrode or a portion of the reference-gas passage in the vicinity of the reference electrode, whereby the pumping cell is relatively efficiently heated by the heater, and its pumping ability is held at a higher level, while at the same time the service life of the heater is prolonged.

While the present invention has been described in its preferred embodiments, and the individual embodiments have been described in sev-

eral forms, for illustrative purpose only, the electrochemical devices of the invention are not limited to the illustrated details of construction and arrangements.

Although the electrochemical devices according to the invention are preferably used as lean-burn sensors as illustrated, the device may be used as a rich-burn sensor for handling a fuel-rich exhaust gas whose oxygen partial pressure is lower than that of the stoichiometric air-fuel ratio, as previously indicated. In this latter instance, the direction of flow of an electric current through the pumping cell is reversed. Further, the electrochemical devices of the invention are equally suitably used as oxygen sensors for detecting exhaust gases which are produced in a combustion process at the stoichiometric air-fuel ratio. In any case, the concentration of oxygen (selected component) of a measurement gas, or the concentration of excess fuel in an exhaust gas is obtained with known methods of measurement. Further, the invention is also embodied as various sensors or controller for determining or controlling the concentration of specific components of a fluid associated with electrode reaction, such as nitrogen, carbon dioxide and hydrogen, other than oxygen.

Claims

1. An electrochemical device for determining the concentration of a component of a gaseous fluid, comprising:

an electrochemical pumping cell (202) including a first planar solid electrolyte body (208) of porous structure having a predetermined diffusion resistance to molecules of said component of the gaseous fluid, and an outer and an inner pumping electrode (210,212) of porous structure disposed in alignment with each other on opposite surfaces of said first solid electrolyte body (208);

an electrochemical sensing cell (204) including a second planar solid electrolyte body (216), a measuring and a reference electrode (218,220) of porous structure disposed on said second solid electrolyte body (216) at least said measuring electrode (218) being disposed on one surface of said second solid electrolyte body (216) on the side towards said first solid electrolyte body (208), said measuring and reference electrodes (218,220) being spaced from each other in a direction parallel to the surface of said second planar solid electrolyte body (216), said measuring electrode (218) being aligned with said outer and inner pumping electrodes (210,212) in a direction perpendicular to said surfaces of said solid electrolyte bodies (208,216);

said outer pumping electrode (210) being exposed to said gaseous fluid, and said inner pumping electrode (212) and said measuring electrode (218) being exposed to substantially the same atmosphere which is introduced from said gaseous fluid through said first porous solid electrolyte body (208), and which contains said component,

a heater layer (206) incorporating a heating element (234) disposed on one side of said second planar solid electrolyte body (216) remote from said first planar solid electrolyte body (208), said heating element (234) being located in alignment with said measuring electrode (218) in a direction perpendicular to said surfaces of said solid electrolyte bodies (208,216); and at least one gastight ceramic layer (224,216;244,216;242,216;216) which substantially completely protects said reference electrode (220) from exposure to said gaseous fluid.

2. An electrochemical device according to claim 1, further comprising a measurement-gas space (252,254,208;208,222) communicating with an outside space in which said gaseous fluid is present, said inner pumping electrode (212) and said measuring electrode (218) being exposed to said substantially the same atmosphere in said measurement-gas space, and further comprising a reference-gas space (246) into which a reference gas is introduced, said reference electrode (220) being exposed to said reference gas in said reference-gas space.
3. An electrochemical device according to claim 2, wherein said measurement-gas space is the porous structure of said first solid electrolyte body (208) which has a predetermined resistance to molecules of said component of the gaseous fluid.
4. An electrochemical device according to any one of claims 1 to 3 wherein a single porous electrode serves commonly as said inner pumping electrode (212) and as said measuring electrode (218).
5. An electrochemical device according to any one of claims 1 to 4, wherein said gastight ceramic layer (242) partially defines a space (246) communicating at one end thereof with the ambient atmosphere, said reference electrode (220) being exposed to said space.
6. An electrochemical device according to claim 1, wherein two said gastight ceramic layers

(224,216) sandwich said reference electrode (220) such that the reference electrode is embedded in said two gastight ceramic layers (224,216).

7. An electrochemical device according to any one of claims 1 to 6, wherein said measuring and reference electrodes (218,220) are disposed on one surface of said second solid electrolyte body (216) on the side towards said first solid electrolyte body (208).
8. An electrochemical device according to any one of claims 1 to 3, wherein said measuring and reference electrodes (218,220) are disposed on opposite surfaces of said second solid electrolyte body (216).

Patentansprüche

1. Elektrochemische Einrichtung zur Bestimmung der Konzentration einer Komponente eines gasförmigen Fluids, enthaltend:
eine elektrochemische Pumpzelle (202), die einen ersten planaren Festelektrolytkörper (208) poröser Struktur mit einem vorgegebenen Diffusionswiderstand gegenüber Molekülen der Komponente des gasförmigen Fluids und eine äußere und eine innere Pumpelektrode (210, 212) poröser Struktur, die miteinander ausgerichtet auf entgegengesetzten Oberflächen des ersten Festelektrolytkörpers (208) angeordnet sind, umfaßt;
eine elektrochemische Fühlzelle (204), die einen zweiten planaren Festelektrolytkörper (216), eine Meß- und eine Referenzelektrode (218, 220) poröser Struktur, die auf dem zweiten Festelektrolytkörper (216) angeordnet sind, umfaßt, wobei zumindest die Meßelektrode (218) auf einer Oberfläche des zweiten Festelektrolytkörpers (216) auf der Seite zu dem ersten Festelektrolytkörper (208) angeordnet ist, die Meß- und Referenzelektroden (218, 220) in einer Richtung parallel zur Oberfläche des zweiten planaren Festelektrolytkörpers (216) voneinander beabstandet sind, die Meßelektrode (218) in einer Richtung senkrecht zu den Oberflächen der Festelektrolytkörper (208, 216) mit den äußeren und inneren Pumpelektroden (210, 212) ausgerichtet ist;
wobei die äußere Pumpelektrode (210) dem gasförmigen Fluid ausgesetzt ist und die innere Pumpelektrode (212) und die Meßelektrode (218) im wesentlichen der gleichen von dem gasförmigen Fluid durch den ersten porösen Festelektrolytkörper (208) zugeführten und die Komponente enthaltenden Atmosphäre ausgesetzt sind;

eine ein Heizelement (234) umfassende, auf einer Seite des zweiten planaren Festelektrolytkörpers (216) entfernt von dem ersten planaren Festelektrolytkörper (208) angeordnete Heizschicht (206), wobei das Heizelement (234) mit der Meßelektrode (218) in einer Richtung senkrecht zu den Oberflächen der Festelektrolytkörper (208, 216) ausgerichtet ist; und
mindestens eine gasundurchlässige Keramikschicht (224, 216; 244, 216; 242, 216; 216), die die Referenzelektrode (220) im wesentlichen vollständig vor einer Exposition gegenüber dem gasförmigen Fluid schützt.

2. Elektrochemische Einrichtung nach Anspruch 1, weiterhin enthaltend einen mit einem äußeren Raum, in welchem das gasförmige Fluid vorhanden ist, kommunizierenden Meßgasraum (252, 254, 208; 208, 222), wobei die innere Pumpelektrode (212) und die Meßelektrode (218) im wesentlichen der gleichen Atmosphäre in dem Meßgasraum ausgesetzt sind, und weiterhin enthaltend einen Referenzgasraum (246), in welchen ein Referenzgas eingeführt wird, wobei die Referenzelektrode (220) dem Referenzgas in dem Referenzgasraum ausgesetzt ist.
3. Elektrochemische Einrichtung nach Anspruch 2, bei der der Meßgasraum die poröse Struktur des ersten Festelektrolytkörpers (208) ist, welcher einen vorgegebenen Widerstand gegenüber Molekülen der Komponente des gasförmigen Fluids aufweist.
4. Elektrochemische Einrichtung nach einem der Ansprüche 1 bis 3, bei der eine einzige poröse Elektrode gleichzeitig als die innere Pumpelektrode (212) und als die Meßelektrode (218) dient.
5. Elektrochemische Einrichtung nach einem der Ansprüche 1 bis 4, bei der die gasundurchlässige Keramikschicht (242) teilweise einen an einem seiner Enden mit der umgebenden Atmosphäre kommunizierenden Raum (246) begrenzt, wobei die Referenzelektrode (220) diesem Raum ausgesetzt ist.
6. Elektrochemische Einrichtung nach Anspruch 1, bei der die zwei gasundurchlässigen Keramikschichten (224, 216) die Referenzelektrode (220) sandwichartig umgeben, so daß die Referenzelektrode in den zwei gasundurchlässigen Keramikschichten (224, 216) eingebettet ist.
7. Elektrochemische Einrichtung nach einem der

Ansprüche 1 bis 6, bei der die Meß- und Referenzelektroden (218, 220) auf einer Oberfläche des zweiten Festelektrolytkörpers (216) auf der Seite zu dem ersten Festelektrolytkörper (208) angeordnet sind.

8. Elektrochemische Einrichtung nach einem der Ansprüche 1 bis 3, bei der die Meß- und Referenzelektroden (218, 220) auf entgegengesetzten Oberflächen des zweiten Festelektrolytkörpers (216) angeordnet sind.

Revendications

1. Dispositif électrochimique pour déterminer la concentration d'un composant d'un fluide gazeux, comprenant :
- une cellule de pompage électrochimique (202) comprenant un premier corps plan en électrolyte solide (208) de structure poreuse possédant une résistance de diffusion prédéterminée aux molécules dudit composant du fluide gazeux, et une électrode de pompage externe et interne (210, 212) de structure poreuse disposées en alignement l'une avec l'autre sur des surfaces opposées dudit premier corps en électrolyte solide (208) ;
 - une cellule de captage électrochimique (204) comprenant un second corps plan en électrolyte solide (216), une électrode de mesure et une de référence (218, 220) de structure poreuse disposées sur ledit second corps en électrolyte solide (216), au moins ladite électrode de mesure (218) étant disposée sur une surface dudit deuxième corps en électrolyte solide (216), du côté vers ledit premier corps en électrolyte solide (208), lesdites électrodes de mesure et de référence (218, 220) étant espacées l'une de l'autre dans une direction parallèle à la surface dudit deuxième corps plan en électrolyte solide (216), ladite électrode de mesure (218) étant alignée avec lesdites électrodes de pompage externe et interne (210, 212) dans une direction perpendiculaire auxdites surfaces desdits corps en électrolyte solide (208, 216) ;
 - ladite électrode de pompage externe (210) étant exposée audit fluide gazeux, et ladite électrode de pompage interne (212) et ladite électrode de mesure (218) étant exposées à essentiellement la même atmosphère qui est introduite par ledit fluide gazeux à travers ledit premier corps poreux en électrolyte solide (208) et qui contient ledit composant,
 - une couche chauffante (206) incorporant un élément chauffant (234) disposé sur un côté dudit deuxième corps plan en électrolyte solide (216) éloigné dudit premier corps plan en

électrolyte solide (208), ledit élément chauffant (234) étant situé en alignement avec ladite électrode de mesure (218) dans une direction perpendiculaire auxdites surfaces desdits corps en électrolyte solide (208, 216) ; et au moins une couche en céramique étanche aux gaz (224, 216 ; 244, 216 ; 242, 216 ; 216) qui protège essentiellement complètement ladite électrode de référence (220) de l'exposition audit fluide gazeux.

2. Dispositif électrochimique selon la revendication 1, comprenant en outre un espace de gaz de mesure (252, 254, 208 ; 208, 222) communiquant avec un espace extérieur dans lequel ledit fluide gazeux est présent, ladite électrode de pompage interne (212) et ladite électrode de mesure (218) étant exposées à ladite atmosphère qui est essentiellement la même dans ledit espace de gaz de mesure, et comprenant en outre un espace de gaz de référence (246) dans lequel un gaz de référence est introduit, ladite électrode de référence (220) étant exposée audit gaz de référence dans ledit espace de gaz de référence.
3. Dispositif électrochimique selon la revendication 2, dans lequel ledit espace de gaz de mesure est constitué par la structure poreuse dudit premier corps en électrolyte solide (208) qui possède une résistance prédéterminée aux molécules dudit composant du fluide gazeux.
4. Dispositif électrochimique selon l'une des revendications 1 à 3, dans lequel une électrode poreuse unique sert communément comme ladite électrode de pompage interne (212) et comme ladite électrode de mesure (218).
5. Dispositif électrochimique selon l'une des revendications 1 à 4, dans lequel ladite couche en céramique étanche aux gaz (242) définit partiellement un espace (246) communiquant à une extrémité de celui-ci avec l'atmosphère ambiante, ladite électrode de référence (220) étant exposée audit espace.
6. Dispositif électrochimique selon la revendication 1, dans lequel deux desdites couches en céramique étanches aux gaz (224, 216) maintiennent en sandwich ladite électrode de référence (220) de sorte que l'électrode de référence est noyée dans lesdites deux couches en céramique étanches aux gaz (224, 216).
7. Dispositif électrochimique selon l'une des revendications 1 à 6, dans lequel lesdites électrodes de mesure et de référence (218, 220)

sont disposées sur une surface dudit deuxième corps en électrolyte solide (216) sur le côté vers ledit premier corps en électrolyte solide (208).

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8. Dispositif électrochimique selon l'une des revendications 1 à 3, dans lequel lesdites électrodes de mesure et de référence (218, 220) sont disposées sur des surfaces opposées dudit deuxième corps en électrolyte solide (216).

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FIG. 1

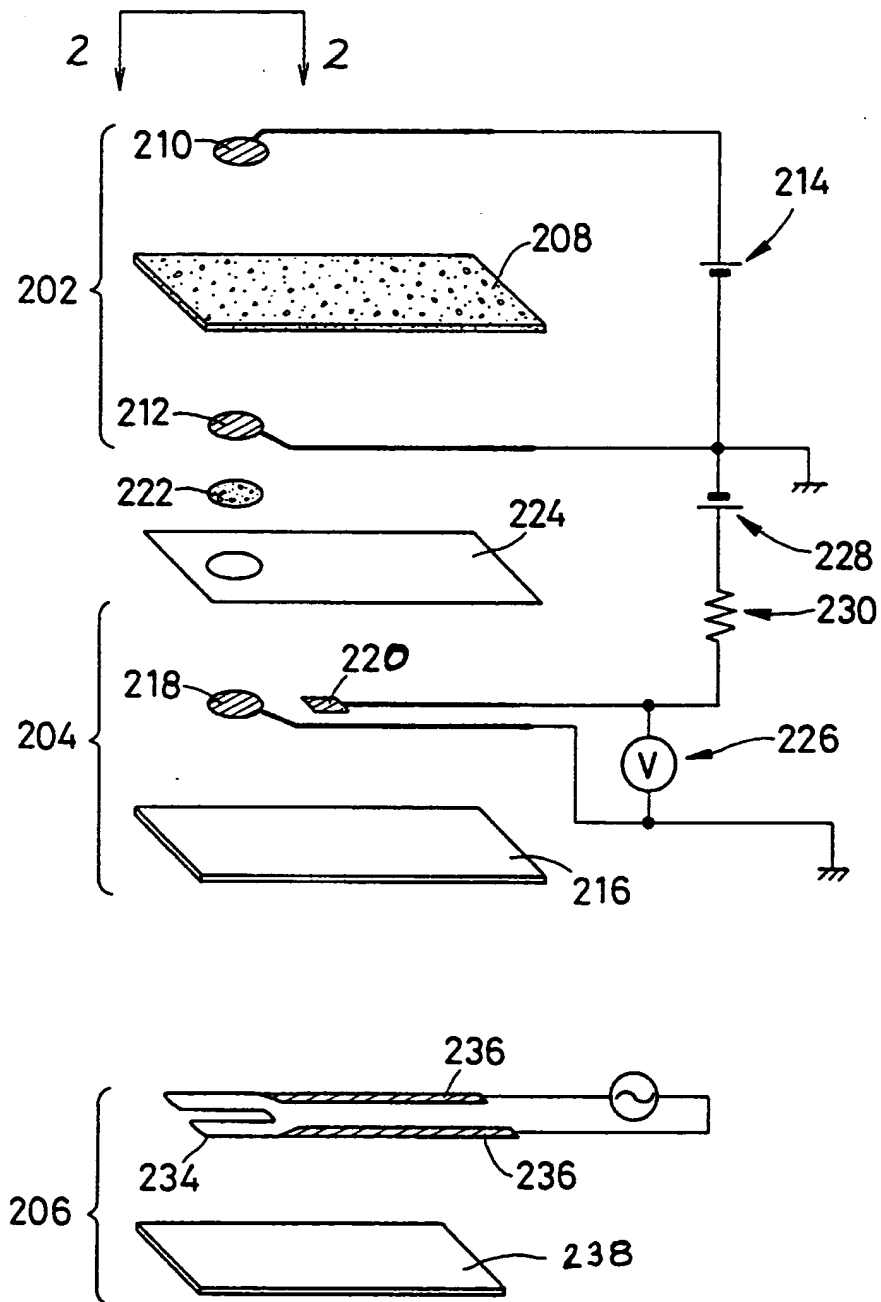


FIG. 2

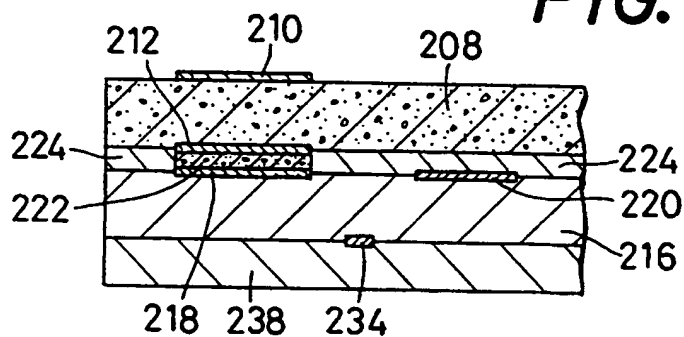


FIG. 4

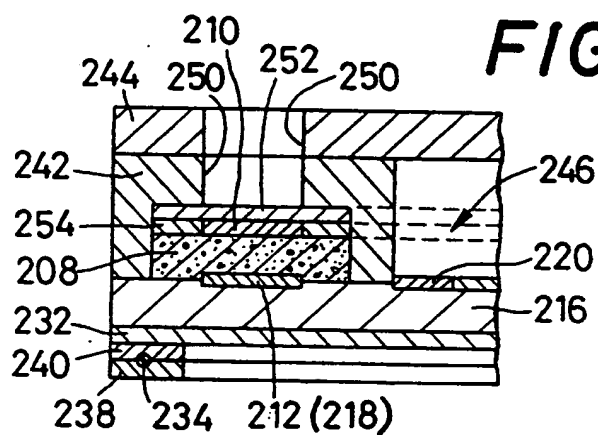


FIG. 5

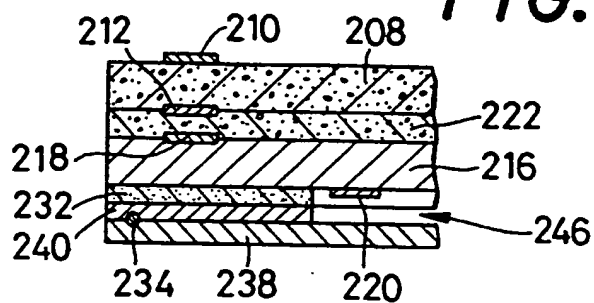
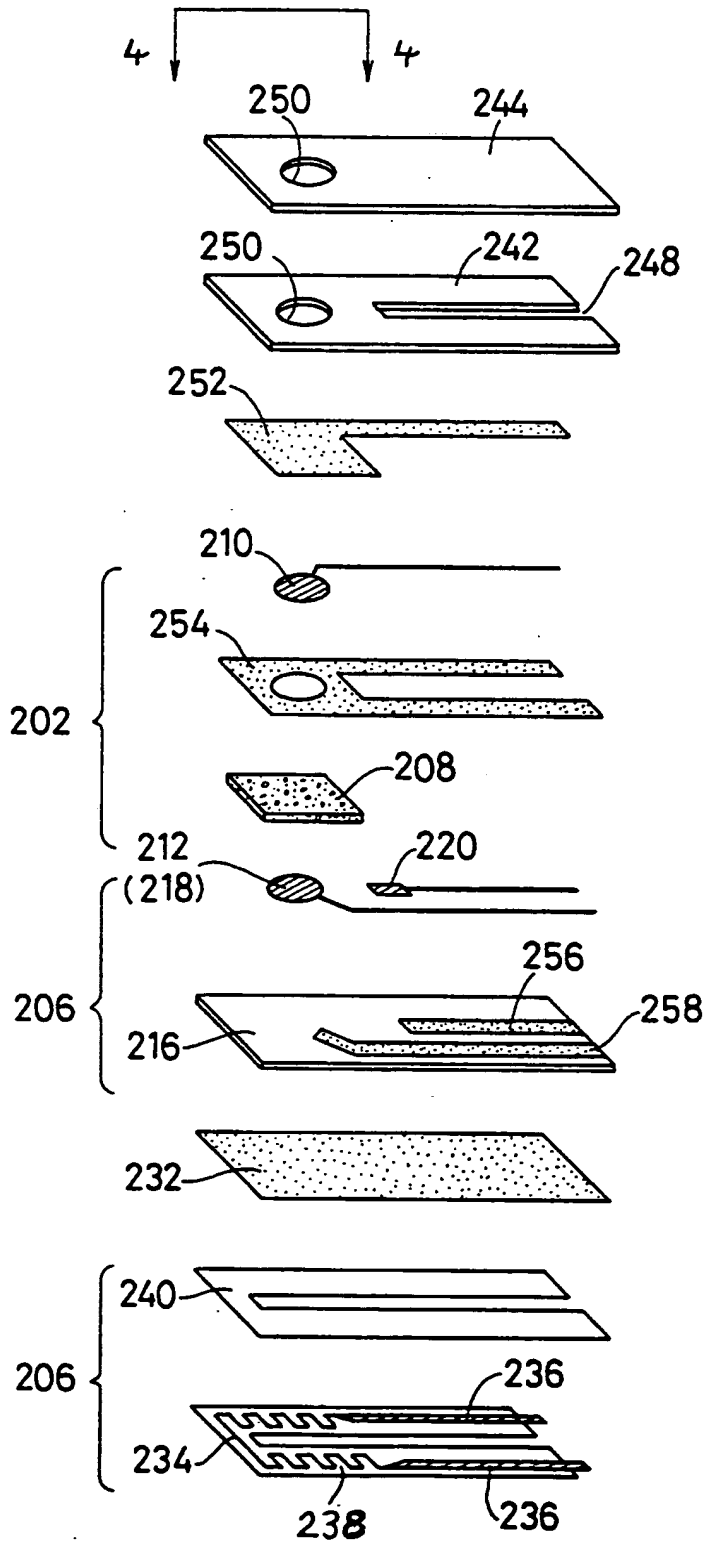


FIG. 3



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